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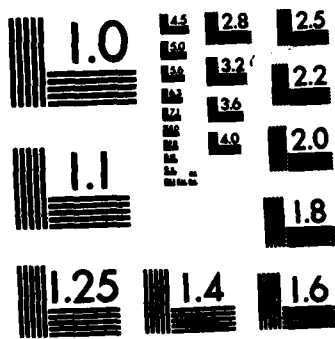
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Electrical Relaxation in Rare Earth

Doped Cubic Lead Fluoride

by

John J. Fontanella and Mary C. Wintersgill

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ELECTRICAL RELAXATION IN RARE EARTH DOPED CUBIC LEAD FLUORIDE*

M.C. WINTERSGILL, J.J. FONTANELLA, F.P. PURSEL
Physics Department, U.S. Naval Academy, Annapolis, MD 21402, USA

and

A.V. CHADWICK, A. AZIMI, V.M. CARR
University Chemical Laboratory, University of Kent at Canterbury, Canterbury,
Kent, UK

and

C.G. ANDEEN
Physics Department, Case Western Reserve University, Cleveland, OH 44106
USA

ABSTRACT

Audio frequency complex impedance measurements are performed over the temperature range 5.5-380K on lead fluoride doped with ten rare earths and lanthanum at various concentrations. It is found that the complexity of the relaxation spectrum increases as the size of the trivalent ion decreases. Specifically, for the largest rare earths, only one relaxation is found. That relaxation is different from the cases in the alkaline earth fluorides where only one relaxation is observed in that the reorientation enthalpy depends strongly upon ion size. Double-doped samples are studied to determine whether the relaxation is due to a simple site or a cluster. For the smallest rare earths, however, at least nine relaxations are found. The concentration studies indicate multiple relaxations for certain sites. Both simple sites and clusters are observed for small rare earths.

INTRODUCTION

Lead fluoride presents a number of interesting differences in its properties as compared with isostructural materials such as the alkaline earth fluorides. In addition to a surprisingly large low frequency dielectric constant which decreases with temperature,¹ it exists in two different structures at room temperature and pressure.^{2,3} Having a relatively low superionic transition temperature,⁴ it has been considered as a candidate for solid electrolyte applications, and therefore the electrical properties of both pure and doped lead fluoride are of considerable interest, and some significant results have been obtained.⁵⁻⁷ The present work is concerned with cubic lead fluoride doped with ten rare earths, lanthanum and the results are compared with similar studies of alkaline earth fluorides.

EXPERIMENTAL PROCEDURE

Single crystals of cubic lead fluoride doped with ten rare earths, lanthanum and yttrium, including six different concentrations of erbium were prepared by the Stockbarger technique⁸ and complex impedance measurements at temperatures between 5.5K and 380K were performed, as described previously.⁹ For each sample, the results were transformed to the complex dielectric constant $\epsilon^* = \epsilon' - \epsilon''$ using techniques described elsewhere¹⁰ and the values of the linear thermal expansion coefficient used were for pure PbF_2 ¹¹ due to a lack of values for rare earth doped lead fluoride.

RESULTS AND DISCUSSION

Rare Earths larger than Gd

There is a striking variation in the dielectric relaxation spectrum, as the dopant ion size changes, as shown in Fig. 1. For larger dopants than gadolinium, in samples with 0.1% dopant, the spectrum is dominated by a single relaxation peak which is considerably stronger than any of the relaxations seen in the AEF. The activation energy of this peak changes steadily by about .04 eV per rare earth from approximately 0.4 eV for La to about 0.1 eV for Gd. This type of behavior has been observed in studies of the alkaline earth fluorides (the R_{IV} relaxation observed in CaF_2 , SrF_2 but not in BaF_2), for a relaxation associated with two rare earths, specifically the "gettered 2:2:2" cluster.^{12,13} In lead fluoride, however, it is the only relaxation observed for large rare earths in contrast to the AEF where at least one other peak is always seen. Thus, it is considered unlikely that the only peak in lead fluoride at the 0.1% doping level should be associated with more than one rare earth. This is supported by the concentration studies which show that from 0.1 to 1.0 mol-% the 70K peak grows at the expense of the 50K peak.

In an effort to clarify this point, the dielectric spectrum of a sample doped with 0.05% each of La and Gd was taken, and is shown in Fig. 2 together with those of La- and Gd-doped samples. The spectrum for the double doped sample is dominated by the same two relaxations (180K, 55K) as are seen in the La- and Gd-doped samples. No corresponding "hybrid" relaxation peak involving both types of dopant ions is observed. Such a peak would be larger in magnitude than the single dopant peaks, and on the basis of earlier AEF studies, the position would be expected to

be close to the Gd peak.¹⁴ This confirms that the single dominant peak seen for large rare earths is due to a simple center. However, as can be seen in Figure 2, several hybrid peaks are observed in the double doped sample (30, 80, 135K). These correspond to the small relaxations observed in the Gd-doped material (20, 75, 100K). There is no evidence of such relaxations in the La-doped material.

Two of the three hybrid peaks (30, 135K) are indeed of larger size than the Gd peaks and are close to the positions of the smaller dopant relaxations. In addition, studies of a different dopant concentration indicate that those peaks increase in height with increased dopant concentration. Therefore, these peaks are associated with centers containing at least two rare earth ions.

For the remaining peak, that at 75K, the possible hybrid peak, that at 80K, is very weak. However, the concentration studies indicate that the 75K peak may be due to the same center as the 20K peak. Thus, since multiple relaxations per site have already been identified in this material and since no analogous relaxation is observed in the La-doped material, it is not surprising that a separate, strong, hybrid peak is not observed for the 75K peak.

Rare Earths Smaller than Gd

As the size of the dopant ion decreases, the complexity of the relaxation spectrum increases, as is the case in the alkaline earth fluorides. The relaxation spectra of five samples doped with small RE's are shown in Figure 1. As an example, nine different peaks can be identified in different concentrations of Er-doped PbF_2 as was shown in a previous paper.⁹ The assignments in that work of two peaks, α_1 ,

(10K and 15.6K) associated with a simple center and three peaks, β_1 , (30K, 70K and 160K) associated with a simple cluster, agree with the selective laser excitation work of Mho and Wright.¹⁵ Of the simple clusters, the peak labeled β_3 at 160K shows a clear dependence on ion size. Thus, it may be that the β relaxations are associated with the "gettered" 2:2:2. Another peak, δ (116K) was also identified as a cluster. The same laser work¹⁵ indicates that the peak labeled γ (50K) and designated as due to a simple cluster in the previous paper⁹ is in fact associated with a single dopant ion, although it does reach maximum peak height at a higher concentration than those labeled α . The concentration dependence must therefore be due to some other effect such as reduction of strain energy. Finally, further analysis of the results has yielded a new peak, η , on the high temperature side of the α_2 peak, (about 19K) which is most prominent at the higher concentrations, suggesting that it too is a cluster of some kind.

The positions of both the peaks due to simple centers and some of the cluster associated centers are unusually low in temperature when compared with the alkaline earth fluorides. This may be due partly to the high polarizability of the lead ion or may even indicate that some of these relaxations involve electronic motion. This latter possibility is supported by evidence from other experiments of the existence of electronic contributions to the conductivity of lead fluoride.⁵

REFERENCES

1. G. A. Samara, Phys. Rev. B13, 4529 (1976).
2. G. A. Samara, J. Phys. Chem. Solids, 40, 509 (1979).
3. J. Oberschmidt and D. Lazarus, Phys. Rev. B21 2952 (1980).
4. W. Schröter and J. Nölting, J. de Phys., 41 C6-20 (1980).
5. R. W. Bonne and J. Schoonman, J. Electrochem. Soc. 124, 28 (1977).
6. V. M. Carr, A. V. Chadwick and R. Saghaian, J. Phys. C., 11, L637 (1978).
7. R. E. Gordon and J. H. Strange, J. Phys. C., 11, 3213 (1978).
8. D. R. Figueroa, A. V. Chadwick and J. H. Strange, J. Phys. C., 11, 55 (1978).
9. J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, A. V. Chadwick, A. Azimi, V. M. Carr, and C. G. Andeen, Proceedings of the Second European Conference on Solid State Chemistry, Veldhoven, The Netherlands, 7-9 June 1982, to be published.
10. C. Andeen, D. Link and J. Fontanella, Phys. Rev. B16 3762 (1977).
11. G. K. White, J. Phys., C13, 4905 (1980).
12. C. G. Andeen, J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, R. J. Kimble, Jr., and G. E. Matthews, Jr., J. Phys., C14, 3557 (1981).
13. M. C. Wintersgill, J. J. Fontanella, P. Welcher, R. J. Kimble, Jr., and C. G. Andeen, J. Phys., C13, L661 (1980).
14. C. G. Andeen, G. F. Matthews, Jr., M. K. Smith, and J. Fontanella, Phys. Rev., B19, 5293 (1979).
15. S. I. Mho and J. C. Wright, private communication.

Figure 1. ϵ'' vs. $T(K)$ for various rare earths and lanthanum in lead fluoride at 10^4 Hz. The concentration is nominally 0.1 mol-%.

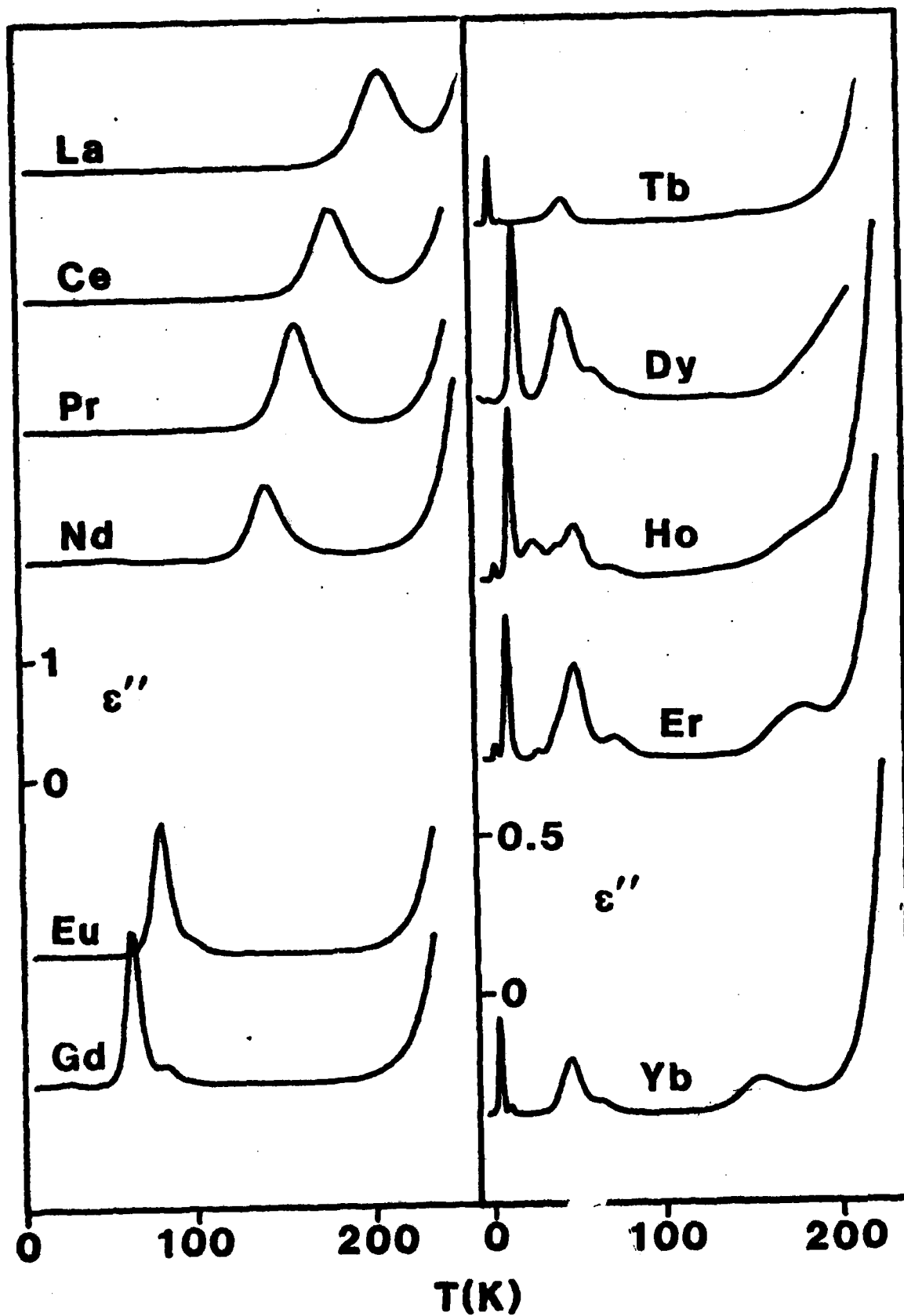
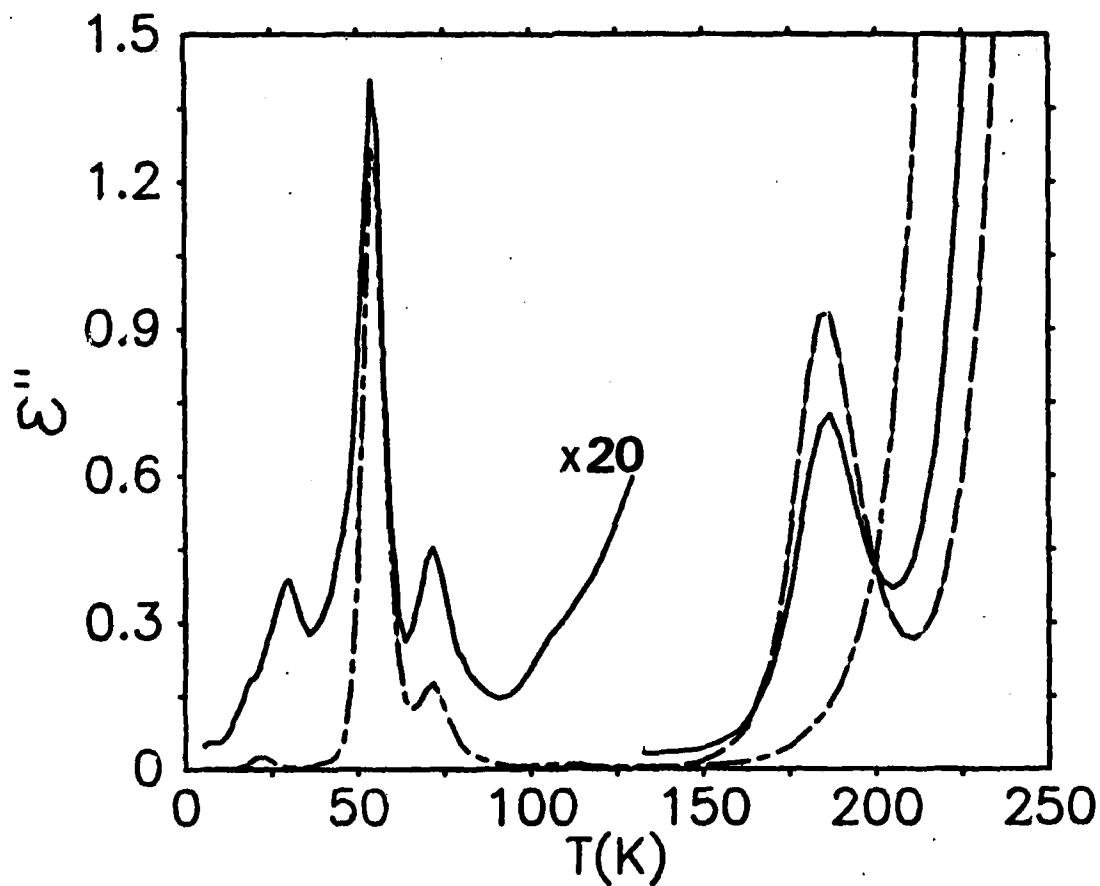


Figure 2. ϵ'' vs. $T(K)$ for 0.2 mol-% Gd (chain link), 0.1 mol-% La (dashed line), and 0.05 mol-% each of Gd and La (solid line) in lead fluoride at 10^3 Hz. (Data for double-doped material is multiplied by 20 for temperatures less than 130K.)



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